Low Temperature Isotope Effect in Ammonium Hexachloroselenate (IV) Studied by ^{35}Cl NQR *

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The temperature dependence of the ^{35}Cl NQR frequency and spin-lattice relaxation time T_{1Q} of $(NH_4)_2SeCl_6$ and $(ND_4)_2SeCl_6$ were measured from 400 K to 24.8 and 53.8 K, respectively. The disappearance of NQR signals in the low temperature region of both salts is attributed to phase transitions. We concluded from the temperature behavior of T_{1Q} just above the transition point that the operative mechanism of the transition is different in these salts: The transition of $(ND_4)_2SeCl_6$ seems to be associated with rotary soft modes, while in the natural salt non-rotary soft modes seem to play an important role at the transition.

Key words: Isotope effect; Spin-lattice relaxation; NQR; Phase transition; Ammonium hexachloroselenate; Deuterated ammonium hexachloroselenate.

Introduction

Many studies on the rotational tunneling in ammonium hexachlorometallates(IV), $(NH_4)_2MCl_6$, have been performed by means of neutron inelastic scattering and nuclear magnetic resonance [1–7]. In these studies a very low potential barrier for ammonium rotation was found. Recently, a so-called "deuterium induced phase transition" was observed in $(ND_4)_2MCl_6$ (M = Pd, Pt, Te) at low temperatures [8–13]. Especially $(ND_4)_2TeCl_6$ undergoes phase transitions at 31.9, 46.8, 48.1, and 88.0 K, whereas $(NH_4)_2TeCl_6$ shows only one transition at 86.7 K [14]. At room temperature, $(NH_4)_2SeCl_6$ crystallizes in the same anti-fluorite type structure as $(NH_4)_2TeCl_6$ [6]. One may expect that the selenium complex shows an analogous strong isotope effect like the tellurium complex. In this paper we investigate molecular motions and phase transitions in ammonium hexachloroselenate by measuring temperature dependences of ^{35}Cl NQR frequencies and spin-lattice relaxation times.

Experimental

$(NH_4)_2SeCl_6$ was prepared by adding ammonium chloride (Wako Pure Chem. Ind. 99.0% purity) to a solution of selenium tetrachloride (Soekawa Chem. 99% purity), both dissolved in hydrochloric acid. The yellow precipitates obtained were dried in a desiccator with diphosphorus pentaoxide and used for the NQR measurement without further purification. The deuterated salt was prepared by the same method using deuterated hydrochloric acid (99.5 atom%) and ND_4Cl (98.0 atom%) purchased from Aldrich Chemical Co. The isotopic purity of the deuterated sample was determined to be 99 atom% by the high resolution ^{1}H NMR intensities measured with a JEOL GSX 270 NMR spectrometer. The X-ray powder diffraction patterns of the natural and deuterated salts at room temperature resembled those of K_2PtCl_6-type cubic crystals.

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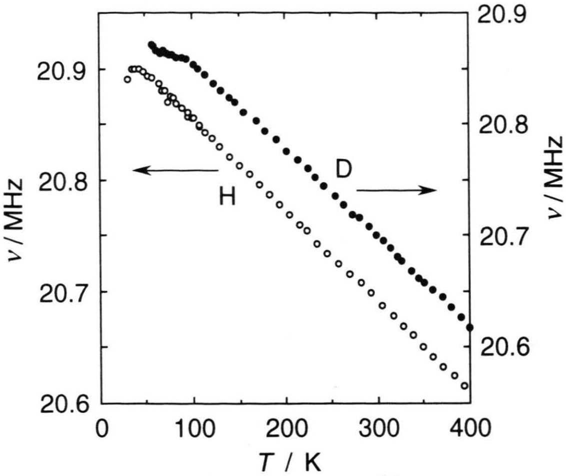

Fig. 1. Temperature dependence of the ^{35}Cl NQR frequency of $(NH_4)_2SeCl_6$ and $(ND_4)_2SeCl_6$.

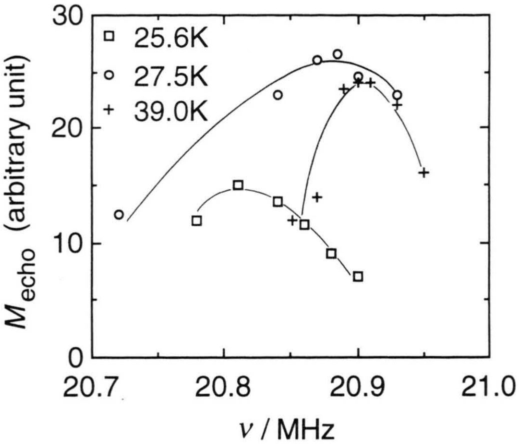

Fig. 2. Plots of the echo-height vs. the irradiated rf frequency for $(NH_4)_2SeCl_6$ at three temperatures.

The temperature dependences of the ^{35}Cl NQR frequency and quadrupole relaxation time T_{1Q} were measured with a Matec pulsed NQR spectrometer described in [15]. T_{1Q} was determined by observing the decay of the echo-height employing the pulse sequence, 180°-τ-90°-τ'-180°, where $\tau' \approx 120$ µs.

Results

Figure 1 shows the temperature dependences of ^{35}Cl NQR frequency of the natural salt (abbreviated ACS) and the deuterated salt (DACS). The frequencies of ACS at 296, 203, and 77 K agree well with reported values [16]. A single NQR line was observed down to 24.8 and 53.8 K for ACS and DACS, respectively, and no signal was observed below these temperatures. Below around 40 K, the free induction decay after a $\pi/2$ pulse could not be observed in ACS, it probably disappeared in the dead time of the spectrometer. The resonance frequencies below this temperature were determined by plotting echo-heights against irradiated rf frequencies as shown in Figure 2, and the rf frequency giving the maximum echo-height was taken to be the resonance frequency at the temperature. The error of the resonance frequency in this temperature region became 100–200 kHz. The temperature dependence of the resonance frequency observed above 90 K for DACS could be explained by the Bayer theory, whereas ACS exhibits a slightly non-linear dependence, as has been observed in several isostructural ammonium salts [17–19]. The temperature coefficients of the resonance frequency, $d\nu/dT$ were -0.86, -0.83, and -0.80 kHz/K in the temperature ranges 70–120 K, 170–220 K, and 300–350 K, respectively.

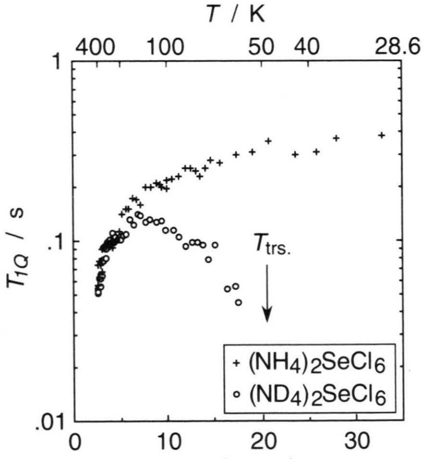

Fig. 3. Temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time T_{1Q} of $(NH_4)_2SeCl_6$ and $(ND_4)_2SeCl_6$.

Temperature dependences of the ^{35}Cl NQR spin-lattice relaxation times in ACS and DACS are shown in Figure 3. It should be noted that T_{1Q} of ACS changes gently as compared with those in the same type of octahedral complexes [20–23]. The T_{1Q} values of the two salts, which were almost equal ($\sim$50 ms, at 400 K) at temperatures higher than ca. 250 K, became different as the temperatures decreases. An anomalous T_{1Q} decrease in DACS was observed upon cooling below ca. 130 K.

Discussion

The disappearance of NQR signal observed in the two salts shows that the environment of the chlorine atoms in these salts at low temperatures is different from that in $(NH_4)_2TeCl_6$, whose NQR signal was observed down to 4.2 K. The signal disappearance has also been reported in the same type of complexes, e.g., $(ND_4)_2TeCl_6$ and $[(CH_3)_3S]_2SeCl_6$ [9, 24]. We propose two possible origins for this phenomenon. One is due to a disorder which gives rise to a distribution of the time-averaged electric field gradient (EFG) causing a broadening of NQR line or leading to a short T_{2Q}^*. It has been reported that some phase transitions are accompanied by this kind of disorder [9]. The other "fade-out" is attributable to a dynamic reason, namely the slowing down of the motions of nearby molecules with decreasing temperature [24]. In this case, the signal disappears because the spin-spin relaxation time (T_{2Q}) becomes too short to get any observable signal. Very recently, a heat capacity measurement proved that ACS undergoes a phase transition at 24.5 K, while DACS undergoes two successive phase transitions at 45.7 and 48.2 K [25]. Since these temperatures are close to those of the fade-out of the NQR signals, the disappearance in ACS and DACS seems to be strongly connected with these phase transitions.

$(NH_4)_2SeCl_6$

The anomalous concaved temperature dependence of the ACS NQR frequency can be explained using the theory proposed by Negita et al. [26]. Making two assumptions on the motion of ammonium ions, they explained why the NQR frequency deviated positively from Bayer's temperature dependence [18, 26]. One of the assumptions is that the contribution from an ammonium ion to the EFG is the time averaged EFG produced by the NH_4^+ ion in the rotating and static states. The other assumption is that the rotating NH_4^+ ion gives a higher resultant EFG at the chlorine nucleus than the static one. With temperature increase, the ratio of the time in rotation to the time at rest becomes larger, so that the slope becomes less negative at high temperatures. Since the moment of inertia of ND_4^+ is twice of that of NH_4^+, this ratio in DACS is smaller than in ACS, consequently the NQR frequency of DACS is less affected by the rotation.

The temperature dependence of ACS T_{1Q} shown in Fig. 3 behaves normal. The least-squares fitting to the T_{1Q} values observed below 140 K was performed by the SALS program [27] using the equation:

$$T_{1Q}^{-1} = a\,T^n\,, \qquad (1)$$

where a and n are fit-constants [28]. The optimal adjustment yielded $a = 0.56\ \mathrm{s}^{-1}\,\mathrm{K}^{-n}$ and $n = 0.45$. Since the contribution from the lattice vibration to the relaxation rate is usually expressed as $T_{1Q}^{-1}\,(\mathrm{vib.}) \sim T^2$ [29], the obtained $n = 0.45$ is too small to be attributed only to the lattice vibration. This indicates the presence of other relaxation mechanisms in ACS, for which we inquire into two possible effects, namely NH_4^+ rotation and phase transition which causes the fluctuation of EFG at chlorine nuclei. It is difficult to estimate directly the contribution to the T_{1Q} from the NH_4^+ rotation (tunneling). T_{1Q} data of $(NH_4)_2PtCl_6$, which undergoes no phase transition and keeps the anti-fluorite type structure down to below 4.2 K, have been reported by Armstrong, et al. [30]. We calculated the power number (n) in $(NH_4)_2PtCl_6$ using the reported data in the temperature range ca. 30–100 K. The difference between the obtained value of $n \approx 1$ and the theoretical value of $n = 2$, which contains only contribution from the lattice vibration, is attributable to the effect from the NH_4^+ ion. The lattice constant of $(NH_4)_2PtCl_6$ smaller than that of ACS [4] implies that the contribution from local charges in NH_4^+ to EFG at chlorine nuclei is larger in $(NH_4)_2PtCl_6$ than in ACS. From these results, the value $n = 0.45$ obtained in ACS smaller than in $(NH_4)_2PtCl_6$ suggests that the EFG fluctuation caused by the phase transition contributes to ACS T_{1Q} in low temperature region. As for the nature of the phase transition, we will discuss later in comparison with that in DACS.

The rapid decrease of T_{1Q} in the high temperature range can be attributed to the reorientation of $[SeCl_6]^{2-}$ ion. The effect of the reorientation on the T_{1Q}^{-1} is expressed as [31]

$$T_{1Q}^{-1}\,(\mathrm{reo.}) = 6\,\tau_0^{-1}\exp(-E_a/k\,T), \qquad (2)$$

where τ_0 and E_a denote the correlation time in the limit of infinite temperature and the activation energy for the reorientation, respectively. This equation means that the larger the E_a becomes, the steeper the slop of the $\ln T_{1Q}$ vs. T^{-1} plot. Although we attempted to fit (2) to the data of the rapid decreasing part of T_{1Q}, the number of data for fitting was too small to obtain a reliable value of E_a. Since the ACS T_{1Q} observed at 400 K is longer than those reported in other similar salts [23, 24, 32], the $[SeCl_6]^{2-}$ reorientation at high temperatures in ACS seems to be slower than in those salts.

$(ND_4)_2SeCl_6$

The temperature dependence of DACS T_{1Q} observed above 250 K is close to that in ACS. This suggests that, as in ACS, the $[SeCl_6]^{2-}$ reorientation is rather slow at 400 K.

The temperature behavior of DACS T_{1Q} observed just above the transition temperature of 48.2 K is different from those in ACS and $(ND_4)_2TeCl_6$ in which T_{1Q} increases with approaching to the transition from high-temperature side [22]. Several R_2MX_6-type complexes crystallizing in the anti-fluorite structure at room temperature undergo displacive phase transitions in which the order parameter is the rotation angle of the octahedral complex ion from the equilibrium orientation in the cubic phase [8, 32, 33]. The T_{1Q} near the transition points in these complexes exhibit a dip caused by softening of the librational mode of the complex ion. The T_{1Q} behavior just above the transition point in these complexes is quite similar to that in DACS. One can, therefore, expect that the transition in DACS is driven by a rotary soft mode of $[SeCl_6]^{2-}$ ions. Bonera et al. have discussed the effect on T_{1Q} of generalized unstable lattice modes near a structural phase transition [34]. For the case of an undamped soft phonon mode, they showed by applying the Cochran's condition on the basis of a Raman two-phonon relaxation mechanism that, if the dispersion curve of the phonon branch can be assumed to be the form $\omega(q) = \omega_0 + \alpha q^2$, where ω and q are the frequency of the lattice vibration and wave number, respectively, the relaxation rate T_{1Q}^{-1} should behave near the transition temperature T_0 as $T^2/(T-T_0)$. Figure 4 is a plot of $T_{1Q}T^2$ against T near T_0 for DACS. The straight line in the figure is a least-squares fit given by

$$T_{1Q}T^2/\mathrm{s\,K}^2 = 22.6\,(T/\mathrm{K} - 50.9)\,. \tag{3}$$

The evaluated T_0 of 50.9 K agrees roughly with 48.2 K determined by calorimetry [25]. T_{1Q} curve expressed as (3) suggests that the phase transition has displacive nature driven by a soft lattice mode [34]. Once can, accordingly, expect from the result of the NQR that the phase transition in DACS is driven by a rotary soft mode of $[SeCl_6]^{2-}$ ions.

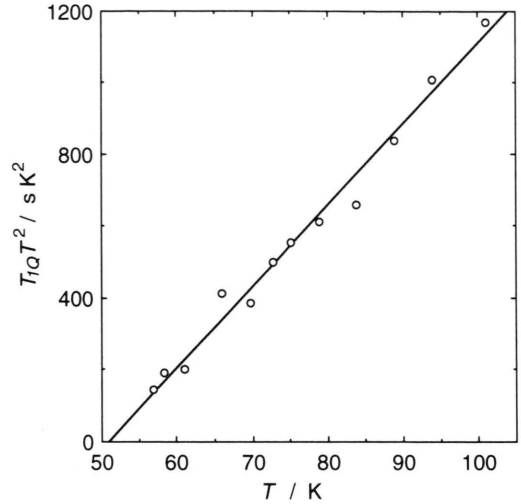

Fig. 4. Plot of $T_{1Q}T^2$ vs. T for $(ND_4)_2SeCl_6$. The solid line represents the least squares fitt.

This interpretation does not contradict the proposed model of order-disorder type first-order phase transition predicted from the large transition entropy of 12.1 J K^{-1} mol^{-1} (Rln 4.3) [25]. In case of methylammonium hexachlorostannate(IV), it was concluded from the calorimetric study that the phase transition is a second-order order-disorder type [35], whereas the neutron diffraction experiment [36] showed the following. Complex ions in the low-temperature phase rotate slightly about the triad axis from the equilibrium orientation in the high-temperature phase, though there exists the orientational disorder of $CD_3ND_3^+$ ion in the high-temperature phase. Temperature dependence of ^{35}Cl NQR spin-lattice relaxation time in this complex salt, which exhibits a deep dip at the transition point, was explained by the rotary lattice mode [32]. These indicate that this phase transition contains two kinds of natures, namely, displacive and order-disorder. In the high-temperature cubic phase of DACS, since the ND_4^+ ion occupies a T_d symmetric site, no disordered structure might be expected. This site is, however, surrounded by twelve chlorine atoms, the immediate neighborhood of ND_4^+ ion is regarded as pseudo-cubic. This means that the ND_4^+ ion is in a disordered state at high temperatures [25]. The phase transition is, therefore, explainable by a rotary soft mode coupled with the ND_4^+ reorientational motion, resulting in the distorted lattice at low temperatures. Cooling through the transition point, a local static disorder is expected to be formed as a result of the frozen motional disorder of the ammonium ions. This can cause the disappearance of the NQR signal in DACS.

On the other hand, the small transition entropy 1.5 $\mathrm{J\,K^{-1}\,mol^{-1}}$ of ACS [25] cannot be attribute to the order-disorder phase transition but a displacive type. This means that motional disorder of the ammonium ion is retained even in the low-temperature phase. The T_{1Q} observed at the transition point is much longer than those in the above mentioned R_2MX_6-type salts having transitions associated with rotary soft modes [30, 32]. Since the rotary lattice mode comprising the complex ion strongly affects the EFG at the chlorine nuclei, the phase transition in ACS should be explained by a mechanism other than the soft mode of rotation origin, probably by a soft mode of another branch.

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